

# WEAKLY NONLOCAL IRREVERSIBLE THERMODYNAMICS - THE GINZBURG-LANDAU EQUATION

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*Dedicated to prof. W. Muschik on the occasion of his 65th birthday.*

**ABSTRACT.** The variational approach to weakly nonlocal thermodynamic theories is critically revisited in the light of modern nonequilibrium thermodynamics. The example of Ginzburg-Landau equation is investigated in detail.

## 1. INTRODUCTION

In the last decades there has been a continuous interest in developing generalized classical continuum theories that are able to describe nonlocal effects. One of the most important (and popular) strategies is to develop so called *weakly nonlocal* continuum theories that is to incorporate higher order space derivatives into the governing equations of continuum physics. The crucial point in this investigations is to clarify the relation of the new equations to the Second Law of thermodynamics.

From that point of view the weakly nonlocal continuum theories can be divided into two groups. The theories in the first group take seriously the thermodynamic requirements and the established structure of continuum physics. We can call them *thermodynamic weakly nonlocal continuum theories*. The theories in the second group does not follow the structure of classical continuum physics and we can call them *variational weakly nonlocal continuum theories* according to the basic method of equation construction. Examples of thermodynamic theories are the so called gradient theory (of thermomechanics) developed by Kosiński and Valanis [1, 2, 3], the virtual power considerations of Germain and Maugin [4], the multifield theory of Mariano [5], a microstructure theory based on the concept of microforce balance of Gurtin [6] and the investigations toward the weakly nonlocal extension of extended thermodynamics by Lebon, Jou and coworkers [7, 8, 9, 10]. Instead of reviewing and criticizing the different approaches our general remark is, that they usually introduce new and disputable new concepts that seem to be too special to serve as foundation of a general nonlocal thermodynamic theory.

The second group is started from the investigations and method introduced by Ginzburg and Landau and constructs a set of prototypical classical weakly nonlocal equations like the Ginzburg-Landau equation and the Cahn-Hilliard equation (see e.g. [11] and the references therein). A unified treatment of weak nonlocality based on this variational approach appears in the so called GENERIC scheme developed by Grmela and Öttinger [12, 13].

The following table compares the different nonlocal theories with theories modeling memory effects according to their basic structural ingredient of nonlocality (in space or time):

	Space	Time
Strongly nonlocal	space integrals	memory functionals
Weakly nonlocal	gradient dependent constitutive functions	rate dependent constitutive relations
Relocalized	???	internal variables

The table is self explanatory, what we should observe is, that all of the weakly nonlocal approaches can be found in the third row of the second column, that is they introduce gradient dependent constitutive quantities (thermodynamic potential, entropy current, conductivity tensor, etc...) to generate the nonlocal effects. It is conspicuous the lacking of the nonlocal counterpart of internal variables.

The main purpose of this paper is to confront the variational approach with the thermodynamic requirements on the example of Ginzburg-Landau equation. In the following section we will review the traditional variational derivation of the Ginzburg-Landau equation. In the second section a Ginzburg-Landau like equation is constructed from thermodynamic principles preserving the compatibility with classical continuum theories. The derivation generalizes the internal variables to nonlocal phenomena and based on a general entropy current. With this method the and the nonlocal constitutive functions can be generated with the help of a force-current system like in classical irreversible thermodynamics [14]. In this way we can eliminate several ad-hoc assumptions of the previously mentioned thermodynamic approaches. The nonlocality of internal variables is generated by thermodynamic requirements and the structure of the theory. In the fourth section a more rigorous derivation, based on the Liu procedure, shows the applicability conditions of the irreversible thermodynamic treatment. From that considerations we can recognize that the previous heuristic thermodynamic derivation is almost completely general under some straightforward physical requirements.

## 2. VARIATIONAL DERIVATION OF THE GINZBURG-LANDAU EQUATION

From a thermodynamic point of view the Ginzburg-Landau equation seems to be the first nonlocal extension of an evolution equation of an internal variable (order parameter, dynamic degree of freedom, etc...). Its traditional derivation is based on the introduction of a gradient dependent thermodynamic potential, a so called (Helmholtz) free energy functional. In the most simple case this thermodynamic potential can be written in the following form

$$(1) \quad \mathcal{F}(\xi) = \int \left( f(\xi) + \frac{\lambda}{2} (\nabla \xi)^2 \right) dV.$$

where  $\xi$  denotes the internal variable, and  $f$  is the 'equilibrium part' of the free energy. According to intuitive thermodynamic requirements we may assume that the equilibrium of the related physical system is characterized by the extremum (minimum) of the above free energy functional. In this case we perform a variation and get the 'functional derivative' of  $\mathcal{F}$  as a generalized intensive quantity conjugated to the internal variable

$$\delta_\xi \mathcal{F} = f'(\xi) - \lambda \Delta \xi.$$

Here the dash denotes a derivative. We can get the *stationary Ginzburg-Landau equation* assuming that this functional derivative is zero

$$f'(\xi) - \lambda\Delta\xi = 0.$$

Introducing a 'relaxational dynamics' we can generate the time dependent Ginzburg-Landau equation as

$$(2) \quad \dot{\xi} = -l\delta\xi\mathcal{F} = -l(f'(\xi) - \lambda\Delta\xi).$$

where  $l$  is a positive scalar coefficient (e.g. in case of scalar internal variable and isotropic material). We may introduce more general free energies, internal variables with different tensorial order, nonisotropic material, etc ...; but the essence of the variational derivations remains the same.

As it was pointed out by Gurtin, the most important problem with that derivations is, that they have nothing to do with the balances of the fundamental physical quantities. He emphasizes the importance of the separation of balances from the constitutive properties: "My view is that while derivations of the form ... are useful and important, they should not be regarded as basic, rather as precursors of more complete theories. While variational derivations often point the way toward a correct statement of basic laws, to me such derivations obscure the fundamental nature of balance laws in any general framework that includes dissipation." [6]

There are three specific problems with the variational approach as a result of the incompatibility with the structure of continuum physics.

- The above derivation is nothing to do with a nonnegative entropy production, e.g. the sign of  $l$  is fixed according to some stability requirements, not by pure thermodynamic conditions.
- The whole equation is not derived from the variational principle, the relaxational dynamics is an additional, independent requirement.
- The whole procedure restrict how the rate terms can appear in the equation. Essentially they can be added by hand waving physical arguments in each specific theory, but experiments and theoretical considerations show well, that they have a typical form, that is independent of the specific theory and a generalized Ginzburg-Landau equation can be written as (see [6] and the references therein)

$$(3) \quad \dot{\xi} = -l(f'(\xi) - \lambda\Delta\xi) + k\Delta\dot{\xi}.$$

Here  $k$  is a positive coefficient.

### 3. THERMODYNAMIC DERIVATION OF THE GINZBURG-LANDAU EQUATION

In this case our task is to find an evolution equation of an internal variable that corresponds to the requirement of nonnegative entropy production. We suppose here that the entropy function depends only on the internal variable and we will use the notation  $\Gamma_\xi := Ds(\xi)$ . If  $\xi = 0$  then  $\Gamma_\xi(0) = 0$ , because  $\xi$  is an internal, dynamic variable. As regards the entropy current we apply the previous physical assumptions also in this case: if  $\xi$  was zero then there is no entropy flow. Moreover, in the light of this assumption and according to the mean value theorem, the entropy current can be written as a linear function of the derivative of the entropy, as in classical irreversible thermodynamics. The coefficient can depend on the internal variable, too:

$$\mathbf{j}_s(\xi) = \mathbf{A}(\xi)\Gamma_\xi.$$

That form of the entropy current was suggested by Nyíri [15]. Therefore the entropy production follows as

$$\sigma_s = \dot{s}(\xi) + \nabla \cdot \mathbf{j}_s = \Gamma_\xi (\dot{\xi} + \nabla \cdot \mathbf{A}) + \mathbf{A} \cdot \nabla \Gamma_\xi \geq 0.$$

We can recognize a force-current structure. In isotropic materials the two terms do not couple and the corresponding Onsagerian equations in the linear approximation are

$$(4) \quad \dot{\xi} + \nabla \cdot \mathbf{A} = l_1 \Gamma_\xi,$$

$$(5) \quad \mathbf{A} = l_2 \nabla \Gamma_\xi.$$

Eliminating  $\mathbf{A}$  from (4) and (5), we get

$$(6) \quad \dot{\xi} = l_1 \Gamma_\xi - \nabla \cdot (l_2 \nabla \Gamma_\xi).$$

Here we have got an equation that is similar to the Ginzburg-Landau equation (2). However, there are some differences.

- At the second term of the right hand side, under the space derivatives there is  $\Gamma_\xi$  instead of  $\xi$ . However,  $\Gamma_\xi$  is a homogeneous linear function of  $\xi$ , being an internal variable.
- The sign of the material coefficients is determined by the Second Law, not by loose stability considerations.
- There is no additional rate term at this level of approximation.
- To extend the derivation to nonlinear and anisotropic cases is straightforward. However, the nonlinearities and anisotropies show a different structure, than in the original equation.

This thermodynamic Ginzburg-Landau equation was derived also by Verhás under some slightly different assumptions, as a governing equation for the transport of dynamic degrees of freedom [16, 17].

**3.1. Generalized thermodynamic Ginzburg-Landau equation.** We can get the generalized form of the Ginzburg-Landau equation at the next level of approximation. A similar equation was received by Gurtin with the principle of microforce balance. In the thermodynamic derivation we consider the previously introduced current intensity factor  $\mathbf{A}$  as an internal variable and follow a similar procedure. For the sake of simplicity we suppose, that the entropy function does not depend on  $\mathbf{A}$ , that is we are not interested in the associated memory effects, we are investigating only the nonlocal extension. The form of the entropy current is similar to that of the Cahn-Hilliard equation [14]:

$$\mathbf{j}_s(\mathbf{A}, \xi) = \mathbf{A} \Gamma_\xi + \mathbf{B}(\mathbf{A}, \xi) \cdot \mathbf{A}.$$

Here  $\mathbf{B}$  is a second order tensor. This form is completely general under the conditions of the mean value theorem, if we exploit that there is no entropy flow when the internal variable  $\mathbf{A}$  is zero. Now the entropy production will be

$$\sigma_s = \Gamma_\xi (\dot{\xi} + \nabla \cdot \mathbf{A}) + \mathbf{A} \cdot (\nabla \Gamma_\xi + \nabla \cdot \mathbf{B}) + \mathbf{B} : \nabla \mathbf{A} \geq 0.$$

It is straightforward to put down the Onsagerian conductivity equations, but after the elimination of  $\mathbf{B}$ , one cannot simplify them further. Therefore, we will treat here only the simplest situation, when the material is isotropic and the approximation is strictly linear (the conductivity coefficients are constants). Now the

conductivity equations are reduced to the following form

$$(7) \quad \dot{\xi} + \nabla \cdot \mathbf{A} = l_1 \Gamma_\xi,$$

$$(8) \quad \mathbf{A} = l_2 (\nabla \Gamma_\xi + \nabla \cdot \mathbf{B}),$$

$$(9) \quad \mathbf{B} = l_3^1 \nabla \circ \mathbf{A} + l_3^2 (\nabla \circ \mathbf{A})^* + l_3^3 \nabla \cdot \mathbf{A},$$

where  $l_1, l_2, l_3^1, l_3^2, l_3^3$  are positive, scalar, constant coefficients. Now a simple calculation eliminates  $\mathbf{A}$  and  $\mathbf{B}$  from the above equations and we get

$$(10) \quad \dot{\xi} = l_1 \Gamma_\xi - l_2 \Delta (1 + l_1 l_3) \Gamma_\xi + l_3 \Delta \dot{\xi},$$

where  $l_3 = l_3^1 + l_3^2 + l_3^3$ . The last term, that is additional to (6) corresponds to the generalized Ginzburg-Landau equation (3). The positivity (positive definiteness in a more general situation) of the material coefficients is ensured by the Second Law. However, we should observe, that this generalization has not changed the characteristic thermodynamic term which differs from the original Ginzburg-Landau form:  $\Gamma_\xi$  stands under the Laplacian instead of  $\xi$ .

We can continue the introduction of new nonlocal internal variables, putting  $\mathbf{B}$  into the basic state space. In this case  $\mathbf{B}$  becomes internal variable and we can introduce a corresponding current intensity factor. Continuing this procedure, we can develop a whole phenomenological hierarchy of weakly nonlocal transport equations of higher and higher orders. The further research in this direction has a special importance for the kinetic theories, because we do not have a well established approximation scheme for nonlocal phenomena like the momentum series expansion in case of memory effects. The outlined phenomenological hierarchy of nonlocal equations can suggest a similar approach for the kinetic equations including the sensitive question regarding the closure of the corresponding relations [18, 19]. It is straightforward to extend the above treatment considering memory and nonlocal effects together.

#### 4. A MORE EXACT DERIVATION OF THE GINZBURG-LANDAU EQUATION

There are some basic problems in the heuristic approach of irreversible thermodynamics that should be addressed in a modern treatment. We can avoid them applying a more rigorous form and exploitation of the Second Law (nonnegative entropy production) that was applied in the previous section. In this section we make a distinction between the state variables and the constitutive quantities at the beginning and we apply the Liu procedure [20, 21].

As we have seen in the heuristic treatment, the thermodynamic Ginzburg-Landau equation was received as a general evolution equation for an arbitrary internal variable with the requirement of the compatibility with the Second Law. Therefore, let us denote our basic state space spanned by an internal variable  $\xi$  with  $Z_\xi$ . We are to find an evolution equation of the internal variable in the form:

$$(11) \quad \partial_t \xi + \mathcal{F} = \mathbf{0},$$

with the requirement of a nonnegative entropy production

$$\partial_t s + \nabla \cdot \mathbf{j}_s \geq 0.$$

Here  $\mathbf{j}_s$  is the entropy current and  $\partial_t$  denotes the partial time derivative. With the different notation of the time derivatives we emphasize that in case of moving media some further considerations are necessary. The constitution space, where the constitutive quantities are defined is spanned by  $\xi$  and its first and second

gradients  $(\xi, \nabla\xi, \nabla^2\xi)$ . Therefore  $C_I = Z_\xi \times \text{Lin}(Z_\xi, \mathbb{R}^3) \times \text{Bilin}(Z_\xi, \mathbb{R}^3)$  is the constitution space of the nonlocal dynamics of an arbitrary scalar internal variable. The constitutive quantities are the entropy, the entropy current and the form of the evolution equation  $(s, \mathbf{j}_s, \mathcal{F})$ . Therefore in the Liu procedure the nonnegative entropy production is supplemented by (11)

$$\begin{aligned}\partial_t\xi + \mathcal{F} &= 0, \\ \partial_1 s \partial_t \xi + \partial_2 s \partial_t \nabla \xi + \partial_3 s \partial_t \nabla^2 \xi + \partial_1 \mathbf{j}_s \cdot \nabla \xi + \partial_2 \mathbf{j}_s : \nabla^2 \xi + \partial_3 \mathbf{j}_s \cdot : \nabla^3 \xi &\geq 0.\end{aligned}$$

According to Liu's theorem there exist a  $\Gamma$ , to be determined from the Liu equations, which can be written in a particularly simple form

$$\begin{aligned}\partial_1 s - \Gamma &= 0, \\ \partial_2 s &= 0, \\ \partial_3 s &= 0, \\ \partial_3 \mathbf{j}_s &= 0.\end{aligned}$$

The dissipation inequality in our case is

$$(12) \quad \partial_1 \mathbf{j}_s \cdot \nabla \xi + \partial_2 \mathbf{j}_s : \nabla^2 \xi - \Gamma \mathcal{F} \geq 0.$$

The solution of the Liu equations gives that  $s$  depends only on the internal variable  $\xi$ ,  $\Gamma = \Gamma_\xi = Ds(\xi)$  is the derivative of the entropy and  $\mathbf{j}_s$  does not depend on the second gradient of  $\xi$ . Unfortunately these considerations do not simplify the entropy inequality at all, we may look additional conditions. We write the entropy current in the following form

$$(13) \quad \mathbf{j}_s(\xi, \nabla\xi) = \mathbf{A}(\xi, \nabla\xi)\Gamma(\xi).$$

Considering the Liu equations we can see again, that this form of the entropy current is completely general. Under some differentiability conditions the entropy inequality turns out to have the same form that we received with the heuristic considerations of the previous section

$$\mathbf{A} \cdot \nabla \Gamma + (\nabla \cdot \mathbf{A} + \mathcal{F})\Gamma \geq 0.$$

Let us remark, that in (12) there are two constitutive quantities (the entropy current and  $\mathcal{F}$ ) and three additive terms. To simplify the inequality for constructing a force current system there is no other choice that we have done here: we should unite two of the terms with some reasonable physical assumption. Assumption (13) is almost purely mathematical, the physical condition is hidden in the differentiability of  $\mathbf{A}$ . But that is necessary for the construction of constitutive functions, because, if  $\mathbf{A}$  is continuously differentiable we can solve the resulted inequality and get the Onsagerian structure.

**Remark 4.1.** *In this procedure we applied the Coleman-Mizel form of the Second Law, with the requirement that the nonnegative entropy production is a consequence of pure material properties, and valid for all (continuously) solutions of the evolution equation on the internal variable [22].*

Let us observe that one of the consequences is that a gradient dependent thermodynamic potential (entropy of free energy) is not compatible with a nonnegative entropy production and a relaxational (or any) kind of evolution equation for the internal variable.

## 5. DISCUSSION AND FURTHER REMARKS

The applied thermodynamic procedure can be applied to receive several other classical weakly nonlocal equations of continuum physics, e.g. the Guyer-Krumhansl equation for nonlocal heat conduction of the Cahn-Hilliard equation for first order phase transitions [23]. The Liu procedure shows well the conditions (that are mostly mathematical).

The differences between the traditional and the thermodynamic form makes possible to compare the consequences of the equations experimentally. Understanding the (space-time) structure generating properties of the original Ginzburg-Landau equation from a thermodynamic point of view seem to be really interesting. Furthermore, we have seen that the experimentally observed additional rate dependent term of the generalized Ginzburg-Landau equation is a natural consequence of the thermodynamic approach. More thorough considerations on the possibilities of variational principles show well that it would be hard to force that rate dependent terms into a variational principle (see e.g. [24, 25]).

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